Photoinduced intramolecular electron transfer in a 2,7-diaminofluorene chromophore decorated with two benzophenone subunits

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An extensive photophysical analysis of a 2,7-bis-(*N*-4-methoxyphenyl-*N*-phenylamino)fluorene derivative covalently linked with two benzophenone moieties is presented. A systematic comparison with a model chromophore without benzophenone was performed. For both chromophores, the electronic properties of the ground states are completely equivalent indicating that benzophenone subunits do not exhibit any electronic interaction with the diaminofluorene core. However, at the singlet excited state, the presence of benzophenones induces the occurrence of additional non-radiative de-excitation pathways. Even the intersystem crossing rate is significantly increased with respect to that of the model one. A photoinduced intramolecular electron transfer (PIET) from diaminofluorene to benzophenone subunits is proposed as the most efficient quenching process. At low polar solvent, the emission of an exciplex confirms the PIET process and the occurrence of a partial charge separation between donor and acceptor parts.

Introduction

Photoinduced intramolecular electron transfer (PIET) leading to a charge separation in a supramolecular structure plays a fundamental role in the dynamics of concomitant processes involved in the photosynthesis, in biology, in photonics or in the solar energy conversion. The simple association of donor and acceptor subunits constitutes an elementary model to address factors inherent to the PIET mechanism.¹⁻⁶ In this case, the electronic structure and the geometric conformation of the excited state are the most important issues. Among the multiple parameters that tune the efficiency of PIET, the distance (d_{AB}) between the donor (D) and the acceptor (A) parts constitutes one of the main decisive variable.7 Its influence has been extensively highlighted.8-11 For instance, the intramolecular electron transfer rate constant (k_{eT}) in a donor acceptor systems that are covalently linked with a rigid non-conjugating spacer^{12–14} shows an exponential decrease with d_{AB} according to the empirical relation: $k_{eT} = A \exp(-\beta (d_{AB} - d_{AB}^0))$. In this expression, d_{AB}^0 denotes the distance of closest approach and β holds information relating to the nature of the linkage and the medium. Such a formalism is less clearly demonstrated for donor-acceptor structures linked by flexible spacers since electron transfer may occur from a wide distribution of excited conformers.⁷ Besides, the conformational dynamics at the excited state as well as molecular environment may promote the charge recombination. One possible strategy to hamper

such a charge recombination is the use of donor and acceptor subunits that can generate intrinsic long-lived radical ions. Focusing on the donor part, the 2,7-diaminofluorene system appears as a potential candidate. This 'push-pull-push' chromophore has attracted attention because of its high interest in nonlinear optical applications.¹⁵⁻¹⁹ Moreover, it is an electron-rich organic compound that should produce a resonance-stabilized radical cation upon oxidation reaction.

Hence in this paper, we characterize the photophysical properties of a 2,7-bis-(*N*-4-methoxyphenyl-*N*-phenylamino)-fluorene derivative linked with two 3-methoxybenzophenone subunits as electron acceptor groups (Scheme 1). The nature and the symmetry of electronic transitions at the ground and excited states are identified from a detailed spectroscopic comparison with the photophysical feature of a model diaminofluorene chromophore without benzophenone moiety. The electronic and conformational influences of the acceptor



Scheme 1 Molecular structures of DAFB and DAF.

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groups toward the photophysics of the chromophore are then discussed.

Experimental

Materials

The synthetic route for the synthesis of both chromophores is depicted in Scheme 2. **DAF** is synthesized from a palladiumcatalysed cross-coupling reaction between 2,7-dibromo-9,9didecyl-9*H*-fluorene and *N*-(4-methoxyphenyl)aniline in toluene using a procedure previously described.^{20,21} The strategy employed for the preparation of **DAFB** first consists in a demethylation of **DAF** using BBr₃ in dichloromethane at -78 °C which leads to phenolic alcohols. A nucleophilic substitution of a bromine atom in 1,2-dibromoethane is carried out in presence of the latter phenolic product with potassium carbonate. Finally, a second nucleophilic substitution of bromine atoms is performed with 3-hydroxybenzophenone using a similar method and leads to **DAFB**.

9,9-Didecyl- N^2 , N^7 -bis-4-methoxyphenyl- N^2 , N^7 -diphenyl-9*H*fluoren-2,7-diamine, DAF. IR(KBr): 695, 749, 819, 830, 1039, 1180, 1242, 1269, 1314, 1440, 1466, 1494, 1507, 1594, 2852, 2925 cm⁻¹. ¹H NMR (C₆D₆, 400 MHz, 295 K): 0.90 (t, J = 7.2 Hz, 6 H), 0.93 (m, 4 H), 1.10 (m, 8 H), 1.24 (m, 20 H), 1.69 (m, 4 H), 3.30 (s, 6 H), 6.74 (d, J = 6.8 Hz, 4 H), 6.86 (t, J = 7.2 Hz, 2 H), 7.13–7.17 (m, 10 H), 7.27 (d, J = 7.8 Hz, 4 H), 7.34 (d, J = 1.6 Hz, 2 H), 7.39 (d, J = 8.3 Hz, 2 H). ¹³C NMR (C₆D₆, 100.6 MHz, 295 K): 14.4, 23.1, 24.6, 29.8, 29.9, 30.1, 30.2, 30.6, 32.4, 40.5, 55.0, 55.3, 115.2, 118.6, 120.3, 122.0, 123.0, 123.2, 127.3, 129.5, 136.3, 141.6, 147.5, 149.2, 152.5, 156.7. HRMS, ESI-MicroTOF, calc. for C₅₉H₇₂N₂O₂, M⁺: 840.5594; found: 840.5671.

9,9-Didecyl-*N*²,*N*⁷-**bis**{**4-[(3-benzoylphenoxy)-ethoxy]phenyl**}-*N*²,*N*⁷-**diphenyl**-*9H*-fluoren-**2,7-diamine DAFB.** IR(KBr): 695, 723, 1072, 1236, 1279, 1317, 1439, 1466, 1492, 1506, 1579,



Scheme 2 (a) Pd₂(dba)₃, PtBu, KotBu, toluene, 70 °C, 16h, 85%. (b) Br₃, CH₂Cl₂, -78 °C, 2h, rt, 87%. (c) BrCH₂CH₂Br, K₂CO₃, EtOH, 60 °C. (d) K₂CO₃, acetone.

1595, 1656, 2852, 2924 cm⁻¹. ¹H NMR (C₆D₆, 400 MHz, 295 K): 0.89 (t, J = 7,0 Hz, 6 H), 0.95 (m, 4 H), 1.11 (m, 8 H), 1.24 (m, 20 H), 1.71 (m, 4 H), 3.76 (m, 8 H), 6.77 (d, J = 8,8 Hz, 4 H), 6.88 (t, J = 7,3 Hz, 2 H), 6.96 (m, 2 H), 6.98 (t, J = 8,0 Hz, 2 H), 7.05 (t, J = 7,4 Hz, 4 H), 7.11–7.18 (m, 12 H), 7.28 (m, 6 H), 7.35 (d, J = 1,5 Hz, 2 H), 7.41 (d, J = 8,1 Hz, 2 H), 7.50 (s, 2 H), 7.78 (d, J = 7,0 Hz, 4 H). ¹³C NMR (C₆D₆, 100.6 MHz, 295 K): 14.4, 23.1, 24.6, 29.8, 29.9, 30.1, 30.2, 30.5, 32.3, 40.5, 55.4, 66.67, 66.70, 114.9, 115.8, 118.6, 119.8, 120.3, 122.2, 123.0, 123.3, 127.2, 128.4, 129.5, 129.6, 130.3 (2C), 132.2, 136.3, 138.3, 139.6, 142.0, 147.4, 149.1, 152.5, 155.6, 159.2, 195.5. HRMS, ESI-MicroTOF, calc for C₈₇H₉₂N₂O₆, M⁺: 1260.6955; found: 1260.6994.

All the solvents employed for photophysical analysis were Aldrich or Fluka spectroscopic grade.

General techniques. The absorption measurements were carried out with a Perkin Elmer Lambda 2 spectrometer. Steady-state fluorescence and phosphorescence spectra were collected from a FluoroMax-4 spectrofluorometer. Emission spectra are spectrally corrected, and fluorescence quantum yields include the correction due to solvent refractive index and were determined relative to quinine bisulfate in 0.05 molar sulfuric acid ($\Phi = 0.52$).²²

The fluorescence lifetimes were measured using a Nano LED emitting at 372 nm as an excitation source with a nano led controller module, Fluorohub from IBH, operating at 1MHz. The detection was based on an R928P type photomultiplier from Hamamatsu with high sensitivity photon-counting mode. The decays were fitted with the iterative reconvolution method on the basis of the Marquardt–Levenberg algorithm.²³ Such a reconvolution technique allows an overall-time resolution down to 0.15 ns. The quality of the exponential fits was checked using the reduced χ^2 (\leq 1.2).

Phosphorescence and steady-state anisotropy measurements were performed in ethanol at 77 K. The samples are placed in a 5-mm diameter quartz tube inside a Dewar filled with liquid nitrogen. Two Glan–Thompson polarizers are placed in the excitation and emission beams. The anisotropy *r* is determined as follows: $r = \frac{I_{VV} - gI_{VH}}{I_{VV} + 2gI_{VH}}$ with $g = \frac{I_{HV}}{I_{HH}}$ Where *I* is the fluorescence intensity. The subscripts denote the orientation (horizontal, H, or vertical, V) of the excitation and emission polarizers, respectively. *g* is an instrumental correction factor. The proper calibration of the set-up was checked using a recent standard method with rhodamine-101 in glycerol.²⁴

Determination of the intersystem crossing quantum yields of chromophores (Φ_{isc}) were performed by a triplet-triplet energy transfer method. Experiments were carried out by laser flash photolysis at nanosecond time scale with an Edinburgh Analytical Instruments LP900 equipped with a 450-W pulsed Xe arc lamp, a Czerny-Turner monochromator and a fast photomultiplier. The samples were irradiated with the third harmonic ($\lambda = 355$ nm, ~10 ns, 5 mJ per pulse) of a Nd/YAG Powerlite 9010 from Continuum. The sample concentration was adjusted to get an absorption of ~0.3 at the excitation wavelength and purged with nitrogen for 15 min prior to photophysical studies. Triplet-triplet energy transfer was performed with camphorquinone (CQ) as energy acceptor

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system. The bimolecular charge transfer process between triplet states of the chromophores and CQ was considered as negligible since the transient absorption spectrum of the long-lived radical cations of chromophores located in 450–550 nm range was not detected. Finally the standard system benzophenone/camphorquinone (BP/CQ) was used to obtain $\Phi_{\rm isc}$. A detailed experimental methodology is described in detail in ref. 16

Ultrafast transient absorption was carried out using the following set-up. A Ti:Sapphire laser system emitting pulses of 0.6 mJ and 30 fs at 800 nm and 1 kHz pulse repetition rate (Femtopower Compact Pro) with home built optical parametric generator and frequency mixers followed were used to excite samples at 370 nm. A white light continuum (390 nm-1000 nm) pulses generated in a 5 mm methanol cell was used as a probe. The variable delay time between pump and probe pulses was obtained using a delay line with 0.1 µm resolution. The solutions were placed in 1 mm circulating cell made from fused silica. White light signal and reference spectra were recorded using a two channel fibre spectrometer (Avantes Avaspec-2048-2). A home-written acquisition and experiment control program in LabView made possible to record transient spectra with an average error less than 10^{-4} of optical density (OD) for all wavelengths. The temporal resolution of our set-up was better than 60 fs. A temporal chirp of probe pulse was corrected by a computer program with respect to a Lawrencian fit of a Kerr signal generated in a 0.2 mm glass plate used in a place of sample.

The cyclic voltammetry experiments (using a computercontrolled Princeton 263A potentiostat with a three-electrode single-compartment cell; a saturated calomel electrode in methanol used as a reference was placed in a separate compartment) were performed at 300 K, in Ar-degassed acetonitrile with a constant concentration (0.1 M) of n-Bu₄BF₄. Ferrocene was used as an internal reference.

The temperature experiments are performed using a cuvette holder provided with a temperature controller (TC 102) from Quantum Northwest. The temperature range is -10 °C to 105 °C.

The optimization of geometrical structures of **DAF** and **DAFB** were carried out in the frame work of the density functional theory (DFT) with the B3LYP/6-31G* basis and using the GAUSSIAN 03 suite.²⁵ To prevent long time calculation and convergence to secondary minima in the potential-energy surface, the long decyl branches were replaced by short ethyl ones. From the time-dependent calculations at TD/MPW1PW91/6-31G* levels, the absorption properties of each chromophore were calculated.

Results and discussion

Ground-state properties

Fig. 1A displays the superimposition of the absorption spectra of both compounds in acetonitrile and Table 1 gathers spectroscopic data in various solvents. The comparison of the absorption spectra indicates that the red part of the spectra is quite similar with two predominant bands located at 300 nm and 375 nm. These bands which are insensitive to solvent



Fig. 1 (A) Absorption spectra of DAF (squares) and DAFB (circles) in acetonitrile. (B) Excitation anisotropies DAF (squares) and DAFB (circles) in glassy matrix of ethanol at 77 K ($\lambda_{em} = 415$ nm).

polarity typically correspond to the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ electronic transitions centered on the diaminofluorene moiety.^{16,26} The existence of such transitions can be revealed by the steady-state excitation anisotropy spectrum which first displays a constant value of *ca*. 0.35 \pm 0.01 within the long wavelength absorption band (Fig. 1B) then decreases and reaches an other plateau with a mean value of *ca*. -0.02 ± 0.02 in the 280–320 nm region in good accordance with literature.²⁶ Hence, the absorption transition moment of the last electronic transition is mainly collinear with the emitting one, and the electronic symmetry of $S_0 \rightarrow S_2$ transition is clearly distinctive from the last one.

These results can be correlated with TDDFT calculations. In Table 2 the energies of the main electronic transitions, the corresponding oscillator strengths and the main orientation of their transition dipole moments are reported. Fig. 2 depicts the HOMO and the LUMO molecular orbitals involved in last electronic transitions of DAF. The first singlet excitation energies at 3.33 eV (373 nm) agree very well with the experimental results. The calculations also indicate that the $S_0 \rightarrow S_1$ transition is a pure HOMO-LUMO transition with a high oscillator strength (f > 1) and involves a symmetrical charge delocalization along the 2,7-bis-(diphenylamino)fluorene bar. Its corresponding transition dipole moment vector (M_{01}) is mainly collinear to the long axis of the fluorene structure.^{27,28} The second absorption band at 305 nm corresponds to two close electronic transitions located at 4.08 eV (304 nm) and 4.11 eV (302 nm). These transitions involve the same set of molecular orbitals and exhibit a similar electronic symmetry. In both cases their transition dipole moment vectors (M_{02}, M_{03}) have their main components in a plane perpendicular to the long axis of the fluorene moiety. Hence the transitions ascribable to the second absorption band clearly exhibit a different electronic symmetry with respect to that of $S_0 \rightarrow S_1$ one.

From Fig. 1, we can also notice that the absorption spectrum of **DAFB** differs from the absorption spectrum of its analogue one below 340 nm. While the last absorption band of the 3-methoxybenzophenones located in the 300-350 nm region is mainly obscured by the absorption of the

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	EOE					
$\begin{array}{cccccccc} \mathbf{DAF} & \lambda_{abs}/\mathrm{nm} & 380 & 380 \\ \lambda_{duo}/\mathrm{nm} & 396 & 399 \\ \Phi & & 0.39 & 0.38 \\ \tau_{fuo}/\mathrm{ns} & 1.07 & 1.01 \end{array}$		TOL	THF	ACN	DMSO	ETOH
Φ Φ 0.39 0.38 0.39 0.38 0.38 0.39 0.38	378 399	381 402	379 404	374 409	378 412	377 404
$\tau_{\rm fluo}/{\rm ns}$ 1.07 1.01	0.43	0.50	0.48	0.52	0.62	0.46
	1.08	0.99	1.14	1.56	1.61	1.21
$k_{\rm r}/10^{-8}$ s ⁻¹ 0.36 0.38	0.40	0.51	0.42	0.33	0.38	0.38
$k_{\rm nr}/10^{-9} {\rm s}^{-1}$ 0.57 0.61	0.53	0.51	0.46	0.31	0.24	0.45
DAFB $\lambda_{\rm abs}/{\rm nm}$ 379 380	377	382	378	370	377	377
$\lambda_{\rm funct}/{\rm nm}$ 395 398	398	401	402	407	411	402
Φ 0.089 0.095	0.064	0.082	0.062	0.051	0.070	0.038
$\tau_{\rm fluo}/{\rm ns}$ 0.29 0.28	0.21	0.19	0.19	0.19	0.23	< 0.15
$k_{\rm r}/10^{-9} {\rm s}^{-1}$ 0.31 0.34	0.31	0.43	0.33	0.27	0.30	
$k_{\rm nr}/10^{-9} {\rm s}^{-1}$ 3.20 3.23	4.57	4.83	4.97	5.02	3.96	

2,7-diaminofluorene moiety, the ${}^{1}L_{a}$ transition of benzophenone derivatives is clearly observed at 250 nm.^{29,30} The extinction coefficient relative to the maximum of last absorption band has a quite similar value for both compounds (~30000 M⁻¹ cm⁻¹), hence the 3-methoxybenzophenone does not seem to induce any interactions with the diaminofluorene moiety at the ground state.

The redox properties of the compounds were characterized by cyclic voltammetry. Fig. 3 shows the cyclic voltammograms for the systems in acetonitrile containing 0.1 M of $(n-Bu)_4 NPF_6$, the cathodic part corresponds to the reversible reduction of 3-methoxybenzophenone moiety, its half-wave potential has a value of ca. -1.78 V versus a standard calomel electrode (SCE) in methanol, perfectly comparable to the reduction potential of benzophenone measured in the same condition within experimental error of ± 10 mV, it thus confirms the absence of electronic interaction between the benzophenone moiety and the donor part. At high potential, each chromophore shows exactly the same set of two reversible oxidation waves; their respective half-wave potentials have a value of 0.55 V/SCE and 0.74 V/SCE. They correspond to the successive one-electron oxidation of the donor subunit leading to the radical cation and the dication both centered in the diaminofluorene part. These radical cations are not sensible to the presence of oxygen since the same voltammograms are obtained in aerated solution. Recently, it has been reported a simple chemical method to obtain radical cations from aromatic amines whose oxidation potentials are below 1.0 V/SCE.^{31,32} The reaction involves the mixing of aromatic amine with copper salt in acetonitrile solution. Fig. 4 shows the evolution of absorption spectrum of DAF in presence of 5 eq. of CuSO₄ in acetonitrile from the time-dependent change observed in the absorption spectra (inset Fig. 4), two kinetic steps are clearly identified. Consecutive to the rapid disappearance of the absorption band of **DAF**, new bands are developing in the 410-560 nm region and in the near infrared region $(\lambda > 900 \text{ nm})$, two isosbestic points are then displayed at 278 nm, 400 nm. This first step corresponds to the formation of the radical cation. In the second step, the absorption band of the radical is markedly decreasing with the concomitant development of a new one in 600-900 nm range. This band is ascribed to the absorption of the dication. The final solution is stable for several hours indicating the persistent character of both oxidized species. A strong stabilizing resonance effect is assumed to explain such a persistent character. The similar reactions are observed with DAFB.

Symmetry and electronic properties of excited states

Fig. 5 shows the normalized absorption spectra and the normalized fluorescence spectra of **DAFB** in solvents of increasing polarity. The Table 1 gathers the photophysical data related to each emitting species. Despite a very slight blue shift observed for the emission band of **DAFB** with respect to the fluorescence of **DAF**, the two chromophores exhibit the same fluorescence band shape. Moreover, in solvents with low dielectric constant ($\varepsilon < 2.5$), the fluorescence spectrum of **DAFB** shows a very weak intensive band in the 500–650 range (inset Fig. 5), the nature of this band will be further discussed.

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 Table 2
 Calculated and observed electronic transitions of chromophores^a

	DAF				DAFB			
	$E_{ m exp}$ ^b /eV	$E_{\rm th}/{\rm eV}$	f	Pol. ^c	$E_{ m exp}$ ^b /eV	$E_{\mathrm{th}}/\mathrm{eV}$	f	Pol. ^c
S ₀ -S ₁	3.32	3.33	1.07	x	3.35	3.32	1.06	x
$S_0 - S_2$ $S_0 - S_3$	4.10	4.08 4.11	0.11 0.33	(y,z) (y,z)	4.08	4.09 4.10	0.23 0.25	(y,z) (y,z)

^{*a*} E_{exp} : Experimental value for the energy of the electronic transition; E_{th} : theoretical value for the energy of the electronic transition; Pol.: main components for the polarization of the electronic transition. ^{*b*} Values in acetonitrile. ^{*c*} *xyz* axes are displayed in Scheme 1.



Fig. 2 Frontier molecular orbitals of DAF.



Fig. 3 Cyclic voltamogramms of DAF (full line) and DAFB (dash-dotted line) in acetonitrile + $(nBu)_4NPF_6$ (0.1 M) on platinum electrode at 200 mV s⁻¹ (concentration of chromophores: 10^{-3} M).

For both chromophores, the zero–zero transition (E₀₀) lies at 3.18 eV and the emission band is hardly shifted to the red region from hexane to DMSO (*i.e.* 980 cm⁻¹). The change in dipole moment between the ground state and excited states, $\Delta \mu_{g-e}$ can be estimated from the $\Delta \nu_{max}$ difference between the maxima of the absorption and fluorescence bands on the basis of Lippert's Δf function and with the assumption that the Onsager cavity has a radius of 5 Å, value obtained from the fully geometry optimization of **DAF** by DFT method. The change in dipole moment from ground to excited state does not exceed 6 D, it thus confirms the weak polar character of the emitting species.¹⁶

DAF and **DAFB** exhibit radiative rate constants (k_r) of same order of magnitude with mean values of *ca*. $0.39 \pm 0.05 \times 10^9 \text{ s}^{-1}$ and $0.32 \pm 0.05 \times 10^9 \text{ s}^{-1}$ respectively. It confirms the electronic equivalency of each excited state. The radiative rate



Fig. 4 Time-dependent changes in the absorption spectrum of DAF (10^{-5} M) in presence of 5 eq. of CuSO₄ (solvent = acetonitrile). Inset: evolution of the absorbance at 480 nm and at 810 nm.

constant value can be directly connected to the square of the fluorescence transition moment $M_{\rm f}$ according to the following equation:^{33,34}

$$k_{\rm r} = \frac{64\pi^4}{3h} n^3 \nu_{\rm f}^3 M_{\rm f}^2$$

Where *n* denotes the refractive index of the medium and $\nu_{\rm f}$ the maximum fluorescence wavenumber (cm⁻¹). The change of the electronic or molecular geometry between the absorption and fluorescence process can also be derived by comparison of the radiative rate constant $k_{\rm r}$ with Strickler–Berg rate constant $k_{\rm r}^{\rm SB}$ calculated from equation:³⁵

$$k_{\rm r}^{\rm SB} = \frac{8\pi c 10^3 \ln 10}{N_{\rm L}} n^2 \nu_{\rm f}^3 \int \varepsilon(\nu_{\rm a}) \mathrm{d}(\ln \nu_{\rm a})$$



Fig. 5 Normalized absorption and fluorescence spectra of **DAFB** in solvents of increasing polarity. Inset: fluorescence of the exciplex in hexane.

In this previous relation, the integrated band absorption spectrum is proportional to the square of absorption transition moment (M_a) as follows:

$$\int \varepsilon(\nu_{\rm a}) d(\ln \nu_{\rm a}) = \frac{8\pi^3 N_{\rm L} n}{3hc 10^3 \ln 10} M_{\rm a}^2$$

where $\varepsilon(\nu_a)$ corresponds to the extinction coefficient at the wavenumber ν_a . Therefore the ratio between k_r and k_r^{SB} leads to ratio of the squared fluorescence and absorption moments. The calculation of k_r^{SB} leads to a value of $ca. 0.33 \times 10^9 \text{ s}^{-1}$ and 0.34 \times 10 $^9~s^{-1}$ for DAF and DAFB, respectively. The ratios $M_{\rm f}^2/M_{\rm a}^2$ exhibit values close to unity (*i.e.* 1.18 for **DAF** and 0.94 for DAFB). Hence, the locally excited state (LE) of each chromophore does not undergo any change in the electronic or conformational structure. The presence of crowded substituents at the rim of the diaminofluorene core does not generate any sterical constraint that could affect the electronic feature of the chromophore at the excited state. Such an assumption is also confirmed by the measurement of the fluorescence anisotropies whose spectra are displayed in Fig. 6. DAF and DAFB exhibit an average value of ca. 0.34 ± 0.03 and 0.36 ± 0.02 , respectively. These results



Fig. 6 Superimposition of the emission spectrum and the emission anisotropy of **DAFB** ($\lambda_{em} = 370$ nm) in glassy matrix of ethanol at 77 K.

clearly indicate that the transition moments for the absorption and for the emission are collinear with the same polarization along the long axis of the 2,7-diaminofluorene moiety.

Moreover, **DAFB** and **DAF** show the same phosphorescence spectrum with a maximum located at 515 nm which leads to a triplet energy of *ca.* 2.41 eV (Fig. 6). In both cases, the corresponding luminescence lifetime is 1.5 s which suggests that the T₁ states have a π,π^* character. The average phosphorescence anisotropy shows values roughly close to 0 in each case, this is consistent with an out-of-plane orientation of the emission moment usually observed for aromatic systems.^{36,37} Indeed the theoretically spin-forbidden T₁ \rightarrow S₀ transition is assumed to be strengthened through vibronic mixing and singlet-state mixing with polarization normal to the molecular plane.³⁶

Intramolecular quenching of singlet locally excited state

The electronic equivalency observed for the S_1 states of **DAF** and **DAFB** singularly contrasts with the large differences of their respective fluorescence quantum yield Φ_{fluo}), for instance Φ_{fluo} of **DAF** is 4 times higher as that of **DAFB** in hexane, and becomes 10 times higher in acetonitrile. The comparison of the non-radiative rate constants (k_{nr}) is also in line with these observations: k_{nr} of **DAFB** is 5 times and 15 times higher than that for **DAF** in hexane and in acetonitrile respectively. Hence, the presence of the 3-methoxybenzophenone subunits in the structure of **DAFB** should lead to additional non-radiative deactivation pathways.

Due to the high-lying proximity of the S₁ state (3.18 eV) with a π,π^* character and the T₁ state of the 3-methoxy benzophenone (3.00 eV) which exhibits an n,π^* character,^{29,30} a first hypothesis that could explain the quenching of singlet state of **DAFB** should be a significant increase of the intersystem crossing (ISC). Table 3 gathers Φ_{ISC} and k_{ISC} for both molecules in apolar and polar solvent. We can notice that k_{ISC} decreases by at least a factor two from hexane to acetonitrile, this is clearly an opposite tendency as that observed for k_{nr} . Even **DAFB** shows a k_{ISC} three times higher than that of its model, the corresponding values are not high enough to assert that ISC constitutes the main non-radiative deactivation route, for instance k_{ISC} in acetonitrile only represents 5% of k_{nr} .

The significant dependence of k_{nr} upon solvent polarity suggests the occurrence of an intramolecular photoinduced electron transfer mechanism (PIET) as a second hypothesis. From the Rehm–Weller formalism, the free energy associated to such a process can be estimated with the following equation:

$$\Delta G_{\rm eT} = E_{\rm ox} - E_{\rm red} - E_{00} + C$$

where E_{ox} and E_{red} correspond to the oxidation and reduction potential of the donor and acceptor respectively, E_{00} is the

	DAF		DAFB	
	$\Phi_{\rm ISC}$	$k_{\rm ISC}/10^{-9}~{\rm s}^{-1}$	$\Phi_{\rm ISC}$	$k_{\rm ISC}/10^{-9} {\rm \ s}^{-1}$
HEX	0.21	0.20	0.17	0.59
ACN	0.14	0.08	0.05	0.26

energy of singlet excited state and *C* is the coulombic energy term characterizing the interaction of the radical ion pairs. This last term can be neglected in a highly polar solvent such as acetonitrile. Assuming a PIET process from the 2,7-diaminofluorene to the 3-methoxybenzophenone moieties, the estimated ΔG_{eT} has a value of *ca*. -0.78 eV in acetonitrile. Therefore PIET is thermodynamically allowed. This is also consistent with the observed fluorescence quenching of **DAF** in presence of increasing amount of benzophenone, the corresponding Stern–Volmer coefficient has a value of *ca*. 52 M⁻¹ in acetonitrile. The quenching reaction leads to a concomitant decrease of the fluorescence lifetime of **DAF** with a dynamic quenching rate constant of *ca*. 3.3 10¹⁰ M⁻¹ s⁻¹ which indicates a diffusion-controlled process.

The occurrence of a PIET process is also supported by the observation of the fully charge-separated state by time-resolved absorption spectroscopy. Pump-probe measurements were performed with excitation at 370 nm promoting the diaminofluorene derivative to its first excited singlet state. Fig. 7 displays the transient spectra of **DAFB** and its model in acetonitrile at 5 ps and 900 ps delays after laser pulse. Both chromophores initially exhibit the same transient absorption bands with a maximum absorption wavelength located at 586 nm. The $S_1 \rightarrow S_n$ absorption of **DAF** relaxed without any spectral changes and the kinetics measured at 600 nm is correctly fitted with a monoexponential (inset Fig. 7A). The obtained decay time (*i.e.* 1.44 ± 0.1 ns) is in close agreement with the lifetime of the S_1 state measured by time resolved fluorescence. However, for DAFB, after the relaxation of the $S_1 \rightarrow S_n$ bands two weak bands are observed until the end of kinetics. The first one which is centered at 505 nm is



Fig. 7 Transient absorption spectra of **DAF** (top) and **DAFB** (bottom) in acetonitrile. Insets: transient absorption kinetics at 600 nm (top) and at 650 nm (bottom).



Fig. 8 (A) Fluorescence spectrum of exciplex in toluene (circles) obtained from subtraction of normalized emission spectra of **DAFB** (full line) and **DAF** (dashed line). (B) Fluorescence decay behaviour of **DAFB** in toluene at 580 nm ($\lambda_{exc} = 372$ nm). The Figure also shows the residuals and the best monoexponential fit to the decay curve.

comparable to the band of the radical cation of **DAF** observed in Fig. 4, the second band localized in 550–750 nm range can be confidently attributed the absorption of the radical anion of the 3-methoxy benzophenone.^{29,38,39} Two components can be extracted from the kinetics measured at 650 nm (inset Fig. 7B), a short-time component (*i.e.* 190 ps) ascribable to S₁ state relaxation and a long-time one whose relaxation time (*i.e.* 1.9 ns) has a value close the detection upper limit of the instrument.

As previously mentioned, the fluorescence band of DAFB shows a weakly intensive shoulder above 500 nm in low polar solvents as hexane, di-n-butylether or toluene. Such a shoulder is totally absent for **DAF**. A broad band is then revealed by subtraction of the normalized emission spectrum of DAFB with its analogue one as shown in Fig. 8A. This band is solvent-dependent and its maximum is clearly red-shifted from hexane to toluene ($\Delta \lambda = 20$ nm). The excitation spectrum measured at 580 nm matches the absorption spectrum of **DAFB** indicating that this new emitting species arises from the chromophore. Moreover, the relative intensity of the band is invariant by increasing the concentration of **DAFB** from 2×10^{-7} M to 1×10^{-5} M which excludes any inter-molecular effect. We can therefore ascribe this band to the emission of an exciplex (E) stemming from the intramolecular charge transfer between the diaminofluorene part and a 3-methoxy benzophenone one. In toluene, the emission contribution of this species correspond to 3% of the total emission which leads to a very weak fluorescence quantum yield of ca. 5 \times 10⁻⁴. As shown in Fig. 8B, the fluorescence intensity collected at 580 nm in toluene decays monoexponentially with an emission lifetime of 4.70 ns. Hence, a precursor-successor mechanism is not evidenced since the decay does not exhibit a second short lifetime component with a negative and opposite preexponential factor.³³ This suggests that the emitting exciplex is not directly provided from the relaxed LE state. Moreover the monoexponential time decay observed for the exciplex indicates that the emission arises from one type of conformers,

generally a parallel sandwich configuration is promoted since it maximizes the overlap of the two charge clouds. From the full geometrical optimized structure of **DAFB** which is depicted in Fig. 9, we can observe a sandwich-like conformation structure between the diaminofluorene moiety and a benzophenone group with a closest inter-aromatic distance of ca. 6.4 Å. The combining factors of large twist angles between aromatic rings linked to the nitrogen atom and the connection on the *meta* position to benzophenone moiety should counterbalance the unfavourable role of the short alkyl linkage. Hence, this structural pre-organization at the ground state should prevent a large amplitude geometrical relaxation at excited state and promote the occurrence of the exciplex emission in low polar solvent. The fluorescence of this exciplex is largely quenched in more polar solvent. This can be ascribed to the formation of a non-fluorescent geminate or solventshared ion-pairs.40

Fig. 10 shows the temperature effect on the fluorescence spectra of each compound. The fluorescence of DAFB is clearly more temperature-dependent than its model fluorophore. Decreasing temperature from 100 °C to 0 °C leads to a fluorescence enhancement of DAFB by a factor of 3.3 while this factor hardly reaches a value of 1.2 for DAF. Interestingly, the fluorescence enhancing of **DAFB** contrasts with the invariance of the exciplex emission (inset to Fig. 10), it confirms the absence of a parent-daughter relationship between the LE and E species. The solvent shell reorganization consecutive to PIET leads the radical-ion pair stabilization. Hence the slow down of solvation dynamics and of the geometrical relaxation at low temperature should hamper PIET leading to the 'switch on' of emission DAFB. Assuming that PIET constitutes the major deactivation pathway, we can derive the relationship:

$$\frac{k_{\rm eT}}{k_{\rm r}^0} = \frac{1}{\Phi} - \frac{1}{\Phi_0}$$



Fig. 9 Optimized ground-state structure of **DAFB** obtained by DFT calculation.



Fig. 10 Temperature effect on the fluorescence spectra of DAF and DAFB in toluene. Inset: invariance of the fluorescence of exciplex upon cooling.



Fig. 11 Arrhenius plot for the substation of the reciprocal quantum yields of **DAFB** and **DAF** (solvent = toluene).

Where k_{eT} denotes the rate constant PIET, k_r^0 is the radiative constant of **DAF**. Φ_0 and Φ are fluorescence quantum yields of **DAF** and **DAFB**, respectively. Only k_{eT} is temperature dependent and with the assumption of an Arrhenius relationship (*i.e.* $k_{eT} = A \exp(-\frac{E_a}{RT})$), activation energy can be measured by temperature effect. Fig. 11 shows the linear relationship between $\ln(\frac{1}{\Phi} - \frac{1}{\Phi_0})$ versus $\frac{1}{T}$. The activation energy related to the association reaction (E_a) is obtained from the slope of the straight line. Hence in toluene, activation energy of *ca*. 9.0 kJ mol⁻¹ is obtained. The value clearly corresponds to the "activation energy" (E_n) of the viscosity of toluene⁴¹ (*i.e.* 8.3 kJ mol^{-1}) and suggests that the rate constant of PIET varies with the temperature in the same way as solvent viscosity. Therefore PIET does not proceed over a significant activation barrier and does not require a large-amplitude conformational change from the locally excited state.

Conclusion

We have characterized the photophysical properties of a 2,7-bis-(*N*-4-methoxyphenyl-N-phenylamino)fluorene derivative covalently linked to two 3-methoxy benzophenone subunits with short flexible spacers. At ground state, the comparison with a model system clearly indicates that the presence of the benzophenone subunits at the rim of the donor core does not affect any of the spectroscopic or electronic characteristics. However at the excited state, a photoinduced intramolecular electron transfer leads to an efficient quenching of the locally excited state. In low polar solvent, the emission of an exciplex confirms the occurrence of a charge transfer process which is also corroborated by the fluorescence switch 'on' of the chromophore at low temperature. The temperature effect also indicates that this quenching pathway does not cross a potential barrier. Hence the conformational preorganization at ground state leads to a weak geometrical relaxation at excited one.

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